2002 ELLIOTT BAY MONITORING

BIOACCUMULATIVE CONTAMINANTS OF CONCERN

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1.0 EXECUTIVE SUMMARY

As part of the 2002 Elliott Bay disposal site monitoring, chemicals that were recently added to the Dredged Material Management Program's draft Lists 1 and 2 Bioaccumulative Contaminants of Concern (BCOCs) were analyzed in selected tissues and sediments. The purpose of this testing was twofold: to determine with what magnitude and frequency these rarely monitored contaminants occur at this disposal site and to ascertain whether standard hazardous waste methods were capable of detecting these compounds at the limits set by the DMMP.

The main conclusions of this study were:

- Most of the new BCOCs were not detected in the sediments and tissues analyzed and those that were detected (PAHs) were at concentrations well below their bioaccumulation trigger values.

- The target trace metals and organic compounds measured in this study can be adequately quantified using routine solid waste methods.

- The semi-volatile data for sediments and tissues were verified using two independent methods (isotope dilution technique and routine analytical hazardous waste methods).

- The analytical applications (e.g., extractions, preparations, raw/fractionated analysis) were generally successful in achieving the DMMP's target detection limits in light of matrix interferences.

- Suggestions for analytical improvements are given for selected analytes

2.0 INTRODUCTION

The Dredged Material Management Program (DMMP) lists bioaccumulative chemicals of concern (BCOCs) in it's sediment testing guidelines for unconfined aquatic disposal at the eight disposal sites in Puget Sound (PSDDA, 2000). If the sediment concentrations of any BCOC exceed the bioaccumulative trigger levels for aquatic organisms established by the DMMP, then the sediment must be evaluated using standardized bioaccumulation tests to determine its suitability for open-water disposal. In 1998, the DMMP initiated a process to revise the BCOC list based on a weight-of-evidence approach that considers recent monitoring data and updated toxicological information. In 2002, the DMMP released the draft revised BCOC lists for public review. Compounds on the draft Lists 1 and 2 were included as analytes in the 2002 Environmental Monitoring Assessment (SEA 2002b) performed by Striplin Environmental associates (SEA).

The primary goal of this testing was to determine if routine hazardous waste analytical methods (e.g., EPA methods 8260, 8270 and 8081) are able to achieve the low-level detection limits required by the DMMP for the new draft List 1 and List 2 BCOC analytes. Additionally, these results serve to document the presence/absence of these infrequently measured compounds in the Elliott Bay disposal area.

This report presents the results from testing of sediments and tissues for various BCOCs from the DMMP's draft Lists 1 and 2. Specifically, sediment and sea cucumber tissue (*Molpadia intermedia*) samples were collected from four perimeter and three onsite stations at the Elliott Bay disposal site, and were analyzed for draft List 1 and 2 BCOC metals, pesticides, and semivolatile compounds using both routine methods and Isotope dilution (e.g., EPA method 1625). A detailed description of the various extraction procedures, fractionation schemes, and instrumentation is provided as well as a discussion of the strengths and shortcomings of these methods. Recommendations for modifications to future testing are also proposed.

3.0 BACKGROUND

At the 2002 Sediment Management Annual Review Meeting (SMARM), the DMMP agencies presented draft revisions to the Bioaccumulative Contaminants of Concern List.[1]. Chemicals were placed on one of the four following lists based on the "reason to believe" that their accumulation in tissues of aquatic organisms could cause a risk to human and/or ecosystem health:

- List 1 – Primary BCOCs (i.e., required for analysis)
- List 2 – Candidate BCOCs (i.e., priority for further analysis)

[1] Draft List 1 and List 2 BCOCs were described in the DMMP Issue paper entitled "*Proposed Revisions to the Bioaccumulative Contaminants of Concern List*," presented at the 2002 Sediment Management Annual Review Meeting (SMARM) (Hoffman 2002). Since the time of this study, the BCOC lists have been further revised. The final lists are reported in an Issue Paper entitled "*Revisions to the BCOC List*," presented at the 2003 SMARM (Hoffman 2003).

- List 3 – Potential BCOCs (i.e., low priority for further study)
- List 4 – Not Currently Considered to be BCOCs

These revisions were developed using a weight-of-evidence approach. This approach used information on detection frequencies from regional monitoring as well as persistence and toxicological information from the refereed literature.

The revision process resulted in substantive changes to DMMP's original List 1 BCOCs (i.e., required for analysis), with over half of the analytes removed and 14 chemicals added to List 1 (6 of which were completely new to the DMMP program). The weight-of-evidence approach also identified 19 chemicals as List 2, candidate BCOCs. While these chemicals have bioaccumulative tendencies and are known as human and ecotoxicants, there is little regional sediment/tissue monitoring information to confirm if they should be included on List 1. Thus, the current study focused on the draft List 2 BCOCs and on draft List 1 BCOCs that were not on the original list[2].

Concurrent with creating the draft lists, the DMMP developed a method table that lists standard and alternative analytical procedures for measuring low concentrations of contaminants in sediment and tissue samples. However, this method table does not proscribe specific digestion and/or extraction procedures for handling matrix interferences that may be associated with the material being analyzed. Likewise, cleanup steps that may be needed to avoid masking the compound being quantified at achievable detection limits are not specified.

4.0 ANALYSIS

Testing of the draft List 1 and 2 BCOCs was conducted on seven sediment and four tissue (i.e., *Molpadia intermedia*) samples[3] that were collected separately, but concurrently, with chemical and biological samples required as part of the 2002 Elliott Bay Environmental Monitoring Assessment (SEA 2002b). Figure 1 shows the station locations. The analytical methods and target detection limits that were required by the DMMP, and the reporting limits of the contract laboratory for each chemical of interest and media are provided in Table 1.

Tissue samples were collected from sea cucumbers that met the size and field-wet weight requirements specified in previous PSDDA disposal site monitoring events (SAIC 1991). The station names and types of analyses conducted for each sample are listed in Table 2. Field replicates were not collected, although analytical replicates were run. Samples

[2] Sediment chemical results and analytical procedures for List 1 BCOC from the original list (e.g., arsenic, silver, nickel, zinc, fluoranthene, benxo(a)pyrene, heptachlor, DDT and PCBs, pentachlorophenol) are provided in the SEA (2002b) report. In addition, because the 2002 Elliott Bay environmental monitoring was carried out as a tiered-partial effort, dioxins/furans and tributyltin were not measured in sediment samples, nor was there an analysis of the original List 1 BCOCs in tissue samples Environmental Monitoring Assessment (SEA 2002b).

[3] Sediment and tissue samples were collected within and adjacent to the dredged material disposal site boundary, perimeter (P) and onsite (S), with the exception of one tissue sample that was collected at a benchmark station (EBB04) sited in deep waters and beyond disposal activity (SEA 2000a).

were stored at the Analytical Resources Inc. (ARI) laboratory at –18°C until time of analysis. Further details of the field sampling procedures and laboratory requirements are provided in the Sampling and Analysis Plan, 2002 Tiered-partial Monitoring in Elliott Bay, Seattle, WA (SEA 2002a).

4.1 DRAFT LIST 1 AND LIST 2 METAL ANALYTES

ARI used EPA methods 6010B, 7131A, 7421, and 7740 for measuring metals concentrations in sediment and tissue samples for both List 1 and List 2 analytes, except for chromium VI and tetraethyltin. ARI measured concentrations of hexavalent chromium (CrVI) and tetraethyltin in sediment and tissue samples using EPA method SM3500 with an alkaline digestion and EPA method 8270 (i.e., GC/MS full-scan approach), respectively. Method SM3500 is similar to DMMP's proposed analytical method, EPA method 7196A/7199, for measuring CrVI concentrations in that both methods perform extractions using alkaline solutions for the analysis. The reason the contract laboratory used the former method is that ARI has established method detection limits (MDL) from in-house studies for its use. The reason for the contract laboratory to run the tetraethyltin analysis along with the other semivolatiles of interest was because of the project's investigative objectives (e.g., managing analyte losses regarding additional manipulations) and the uniqueness of this analyte.

Further details regarding the analytical procedures as they relate to the required DMMP's detection limits are described in Section 4.3. A summary of the sediment and tissue analysis by station is in Appendix B (available on request). Since the laboratory analysis included non-standard PSDDA chemicals, the level of quality assurance (QA) review equivalent to PSDDA QA1 was achieved by comparing laboratory summary results to the required PSDDA QA acceptance limits. This review determined that the data are of good quality and suitable for use in addressing the study's objectives. QA memoranda and the entire QA1 data package are in Appendix A (available on request).

Table 1. Sediment and Tissue Analytical Methods, DMMP's Target Detection Limits (TDL), and ARI's Reporting Limits (RL) for each Analyte from DMMP's Draft BCOC List 1 and 2.

		SEDIMENT		TISSUE	
	Method	**DMMP TDL**	**ARI RL**	**DMPP TDL**	**ARI RL**
List 1 ANALYTES					
		(mg/kg, dry weight)		**(mg/kg, wet weight)**	
Cadmium	SW846 M.7131A	0.04	0.02	0.04	0.04
Chromium (total)	SW846 M.6010B	0.5	0.5	0.5	0.1
Copper	SW846 M.6010B	0.5	0.2	0.5	0.04
Lead	SW846 M.7421	0.1	0.1	0.1	0.1
Selenium	SW846 M.7740	0.2	0.2	0.2	0.2
		(ug/kg, dry weight)		**(ug/kg, wet weight)**	
Alpha-benzene hexachloride	SW846 M.8081	0.1-1.0	0.5	0.25-2.5	1.2
Anthracene	M.1625/8270	2-20	59	5–50	37
Benzo(a)anthracene	M.1625/8270	2-20	69	5–50	42
Endrin	SW846 M.8081	0.2-2.0	1.0	0.5-5.0	2.5
Lindane	SW846 M.8081	0.1-1.0	0.5	0.25 - 2.5	1.2
Heptachlor epoxide	SW846 M.8081	0.2-2.0	0.5	0.5-5.0	1.2
Parathion	M.1625/8270	2.5	23 - 35	5.0	24 - 30
Pyrene	M.1625/8270	2.0-20	59	5–50	37
Toxaphene	SW846 M.8081	5.0-50	100	12-125	250
List 2 ANALYTES		**(ug/kg, dry weight)**		**(ug/kg, wet weight)**	
1,2,4,5-Tetrachlorobenzene	M.1625/8270	2.0-20	43 - 63	5–50	22 – 25
4-Nonylphenyl (branched)	M.1625/8270	2.0-20	20 - 30	5.0–50	18 – 21
Benzo(e)pyrene	M.1625/8270	2.0-20	72	5.0–50	43
Biphenyl	M.1625/8270	2.0-20	41	5.0–50	33 - 36
Chromium VI	SM3500Cr-D Mod.	0.01-0.1	0.14 – 0.28	0.05-0.2	-----
Dacthal	SW846 M.8081	0.1-1.0	1.0	0.25–2.5	2.5
Endosulfan I	SW846 M.8081	0.1-1.0	0.5	0.25–2.5	1.2
Endosulfan II	SW846 M.8081	0.1-1.0	1.0	0.25–2.5	2.5
Heptachloronaphthalenes	M.1625/8270	3–30	10	5–50	5
Hexachloronaphthalenes	M.1625/8270	3–30	10	5–50	5
Kelthane	SW846 M.8081	1.0-10	1.0 – 5.3	2.5–25	2.5
Octachloronaphthalenes	M.1625/8270	3–30	10	5–50	5
Oxadiazon	SW846 M.8081	2.0–10	1.0	5.0–20	2.5
Perylene	M.1625/8270	2.0–20	72	5.0-50	43
Pentabromodiphenyl ether	M.1625/8270	2–20	55 - 140	5-50	73 - 78
Pentachloronaphthalenes	M.1625/8270	3–30	10	5–50	5
Tetrachloronaphthalenes	M.1625/8270	3–30	10	5–50	5
Tetraethyltin	M.1625/8270	6.0	36	50	24
Trichloronaphthalenes	M.1625/8270	3–30	10	5–50	5
Trifluralin	SW846 M.8081	1.0-5.0	1.0	2.0-20	2.5

Notes:

DMMP – Dredged Material Management Program

EPA Method SW846, Test Methods for Evaluating Solid Waste Physical/Chemical Methods (EPA 1986, 1995)

DMMP TDL – Target Detection Limit. For Method 8270 compounds, MDLs are based on two 35-gram extracts (assuming 70% total solids).

ARI RL – Contract laboratory's reporting limit using EPA method 1625 (equivalent to a Practical Quantitation Limit).

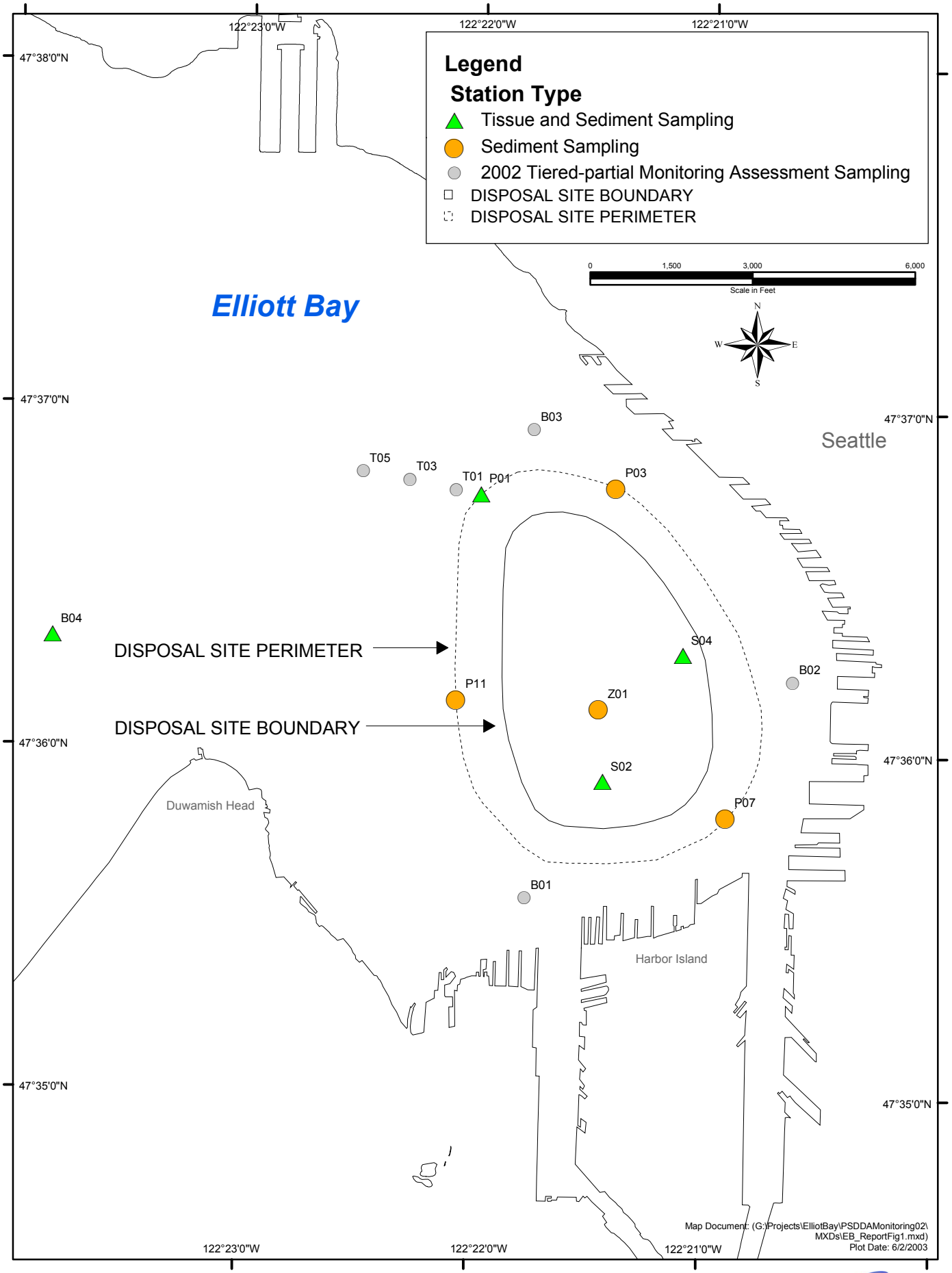

Figure 1. Elliott Bay 2002 Tiered-partial Monitoring Stations Used for the Bioaccumulative Contaminants of Concern Confirmatory Project.

Table 2. Analyses for Each Station Type.

Station Type	Station	Analyses
Onsite	EBS02 and EBS04	DMMP draft List 1 and 2 BCOCs in sediment and tissue samples.
Perimeter	EBP01, EBP03, EBP07, and EBP11	DMMP draft List 1 and 2 BCOCs in sediment samples only (with the exception of EBP01). Sediment and tissue from EBP01 were analyzed for List 1 and 2 BCOCs.
Benchmark	EBB04	DMMP draft List 1 and 2 BCOCs tissue only.

4.2 DRAFT LIST 1 AND 2 PESTICIDE ANALYTES

EPA method 8081 was employed to measure draft List 1 and 2 pesticide concentrations in sediment and tissue samples, with the exception of the compound parathion. For this chemical, analytical procedures described in Section 4.3 were used because the compound is not routinely analyzed by contract laboratories at the low detection levels required by DMMP. To meet the target detection limits, ARI performed an organic extract cleanup on the sediment and tissue samples using Florisil™ chromatography.

Appendices C and D summarize by station the sediment and tissue laboratory analysis of the pesticide analytes. Like metals, the analysis included non-standard PSDDA chemicals; therefore, the level of QA review equivalent to PSDDA QA1 was achieved by comparing laboratory summary results to the required PSDDA QA acceptance limits. This review determined that the data are of good quality and suitable for use in addressing the study's objectives. QA memoranda and the entire QA1 data package are in Appendix A (available on request).

4.3 DRAFT LIST 2 SEMIVOLATILE ANALYTES

Since many of the List 2 SVOAs have rarely (if ever) been analyzed in Puget Sound sediments using standard methods, there was uncertainty about how easily they could be identified and recovered, whether they would co-elute with other analytes, and how representative the surrogates would be of the target chemicals. Furthermore, extraction and/or clean-up procedures can reduce analyte recoveries. To address these issues, a modified version of EPA Method 1625 (*Semivolatile Organics by Isotope Dilution HRGC/HRMS* - EPA 1989) was used to validate the data obtained by the recommended hazardous waste-type analysis (EPA method 8270C) for tissue and sediment. Additional sample processing methods (e.g., accelerated solvent extractions, fractionation steps, hi-resolution GPC clean-ups) were used to remove matrix interferences and enhance the ability to recover semivolatile analytes at very low concentrations.

Isotope dilution is a form of matrix spike for all the target compounds in a sample. A known quantity of labeled isotope is added to the sample enabling one to track and correct the target analyte concentration based on isotope recoveries measured with a mass spectrometer. Using isotope dilution, one can determine how the analyte is responding in different phases of the analysis related to sample manipulations (i.e., cleanups, preparations, etc.) and extraction procedures. The method is also used to substantiate the target analytes' identity concurrent with evaluating the applicability of an alternate analysis (EPA method 8270C), via comparing of ion profiles.

To meet required DMMP's target detection limits, various organic extract cleanups were used to remove selected compounds that can interfere with the target analytes (sulfur, petroleum, etc.). These included a sulfur removal method for sediments and extract fractionation by normal phase (i.e., silica gel) chromatography for sediment and tissue samples. Thus, stable isotope labeled analogs (EPA method 1625) were use to identify any potential losses of target analytes from extract treatments. The labeled analogs used for the GC/MS analysis, as well as details of the aforementioned approach, are in Appendix E (i.e., DMD Technical Memorandum – available on request). Details of analytical reporting requirements are provided in Table 1.

A complete summary of the sediment and tissue laboratory analysis by station and List 2 semivolatile analytes is also provided in Appendices C and D. Because analysis included non-standard PSDDA chemicals, the level of QA review equivalent to a PSDDA QA1 was achieved by comparing laboratory summary results to the required PSDDA QA acceptance limits. This review determined that the data are of good quality and suitable for use in addressing the study's objectives. QA memoranda and the entire QA1 data package are in Appendix A (available on request).

5.0 RESULTS AND DISCUSSION

The use of selected techniques for the analysis of sediment and tissue samples allowed for the determination of analytes of interest at or near DMMP's target detection limits (TDL). Tables 3 and 4 summarize the concentrations of the metals and semivolatile organic compounds from the analyses. Reported concentrations for the halowaxes, parathion, trifluralin, 1,2,4,5-tetrachlorobenzene, pentabromodiphenyl ether, biphenyl, and nonylphenol, have been adjusted and normalized to the recoveries exhibited by the stable isotope labeled analogs[4]. Appendices C and D contain laboratory summary and raw data results from test and blank samples, such as instrumentation calibrations and record logs, for these target analytes.

5.1 ONSITE AND PERIMETER SEDIMENTS

5.1.1 Metals

As shown in Table 3, selenium concentrations (i.e., in dry weight) ranged from 0.4 to 0.6 mg/kg among stations EBS02, EBS04 and EBP01, while concentrations at the remaining stations were reported as non-detects at 0.2 mg/kg. Excluding hexavalent chromium, TDLs for metals were achieved using stated methods. Hexavalent chromium concentrations were undetected (0.14 to 0.28 mg/kg) at all stations. However, TDLs (0.01 – 0.1 ug/kg dry weight) for this analyte could not be reached using the required DMMP analytical techniques, partly because of background interferences from organic carbon, sulfur, and/or iron. These compounds, which are naturally occurring in sediments, can quickly reduce hexavalent chromium to its trivalent state (i.e., stable form). Furthermore, the alkaline extraction method used in this analysis also reduced hexavalent chromium to its trivalent form.

5.1.2 Pesticides

All of the draft targeted pesticide analytes were reported as being non-detects (see Table 3)[5]. Pesticide reporting limits were toward the lower end of the DMMP TDL's, with the exception of the compounds kelthane, parathion, and toxaphene. The variability observed in the kelthane (EPA method 8081; GC/ECD) reporting limits was initially believed to be associated with interferences from polychlorinated biphenyls compounds. Since the review of chromatography scans showed no co-elution issues associated with the reported kelthane measurements, recoveries of kelthane were then examined. Recoveries were greater by EPA method 1625 (GC/MS) than GC/ECD, suggesting that various

[4] This is not a standard DMMP analytical practice; however; because of the additional information from the isotope dilution technique, the DMMP agencies agreed to use the data as correction factors to adjust the concentrations of the draft Lists 1 and 2 BCOC analytes to "based-on-facts" values.

[5] Note that isotope dilution was performed only for those List 1 BCOCs that were newly added (as well as all List 2 BCOCs). Compounds such as PCBs and DDT which were on the original BCOC list were only analyzed using typical solid waste analysis (e.g., Method 8081).

Table 3. Sediment BCOC Concentrations in 2002 Elliott Bay Samples.

Parameter	Proposed PSDDA Sediment BT	Method	EBZ01 Onsite van Veen	EBS02 Onsite van Veen	EBS04 Onsite van Veen	EBP01 Perimeter van Veen	EBP03 Perimeter van Veen	EBP07 Perimeter van Veen	EBP11 Perimeter van Veen	*EBB04 Benchmark van Veen
Conventionals										
Total Solids (%)	---	PSEP 1986	72.6	43.1	38.5	40.3	69.3	54.5	55.4	34.5
Total Volatile Solids (%)	---	PSEP 1986	2.6	5.7	7.8	8.6	2.9	4.5	5.4	5.7
Total Organic Carbon (%)	---	M.9060	2.4	1.9	1.9	1.6	1.1	1.7	1.3	1.8
Ammonia (mg-N/kg)	---	Plumb 1981	16	19	25	4.9	1.8	4.1	1.1	15
Sulfides (mg/kg)	---	PSEP 1986	88	15	18	16	14	17	11	21
Particle Size Analysis		ASTM D422								
Gravel (%)	---		33.4	1.2	0.3	1.7	2	3.1	2.5	0.1
Sand (%)	---		32.6	28.7	14	26.7	68.5	48.5	59.9	22.6
Silt (%)	---		21.4	51.9	63.4	46.8	24.3	38.6	26	50.2
Fines (%)	---		34	70.1	85.7	71.6	29.5	48.4	37.6	77.4
Clay (%)	---		12.6	18.2	22.3	24.8	5.2	9.8	11.6	27.2
PRIMARY ANALYTES										
Metals										
Cadmium	0.04	M.7131A	0.64	0.8	0.54	0.3	0.12	0.25	0.14	
Chromium (total)	0.5	M.6010B	34.8	36	40	42	29	26.1	27.8	
Copper	0.5	M.6010B	45.9	63.1	60.6	44.1	23	49.8	29.8	
Lead	0,1	M.7421	36	46	54	38	22	45	21.2	
Selenium	0.2	M.7740	0.3 U	0.5	0.6	0.4	0.2 U	0.3 U	0.3 U	
PAHs										
Anthracene	2.0 - 20	M.1625/8270	270	239	395	245	109.5	309.7	132	
Benxo(a)anthracene	2.0 - 20	M.1625/8270	370	389	437	728	189.2	543.5	290.9	
Pyrene	2.0 - 20	M.1625/8270	1400 J	1076 J	1136 J	908 J	341	1145.8 J	600.8	
Pesticides										
alpha-BHC	0.1 - 1.0	M.8081	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	
Endrin	0.2 - 2.0	M.8081	1 U	1 U	1 U	1 U	1 U	1 U	1 U	
gamma-BHC	0.1 - 1.0	M.8081	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	
Heptaclor expoxide	0.2 - 2.0	M.8081	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	0.5 U	
Parathion	2.5	M.1625/8270	18 U	31 U	29 U	29 U	31.6 U	29.1 U	34.7 U	
Toxaphene	5.0 - 50	M.8081	98 U	98 U	99 U	98 U	100 U	98.1 U	98.5 U	
CANDIDATE ANALYTES										
Metals										
Chromium VI	0.01 - 0.1	SM3500-mod	0.16 U	0.24 U	0.28 U	0.25 U	0.14 U	0.19 U	0.19 U	
HPAHs										
Benzo(e)pyrene	2.0 - 20	M.1625/8270	260	423	523	397	200.8	626.7	279.9	
Perylene	2.0 - 20	M.1625/8270	440	270	401	310	239.7	338.8	152.9	

Table 3. Sediment BCOC Concentrations in 2002 Elliott Bay Samples.

Parameter	Proposed PSDDA Sediment BT	Method	EBZ01 Onsite van Veen		EBS02 Onsite van Veen		EBS04 Onsite van Veen		EBP01 Perimeter van Veen		EBP03 Perimeter van Veen		EBP07 Perimeter van Veen		EBP11 Perimeter van Veen		*EBB04 Benchmark van Veen
Polychlorinated naphthalenes (Halowaxes)																	
Trichloronaphthalenes	3.0 - 30	M.1625/8270	10	U	10	U	10	U	10	U	10	U	10	U	10	U	
Tetrachloronaphthalenes	3.0 - 30	M.1625/8270	10	U	10	U	10	U	10	U	10	U	10	U	10	U	
Pentachloronaphthalenes	3.0 - 30	M.1625/8270	10	U	10	U	10	U	10	U	10	U	10	U	10	U	
Hexachloronaphthalenes	3.0 - 30	M.1625/8270	10	U	10	U	10	U	10	U	10	U	10	U	10	U	
Heptachloronaphthalenes	3.0 - 30	M.1625/8270	10	U	10	U	10	U	10	U	10	U	10	U	10	U	
Octachloronaphthalenes	3.0 - 30	M.1625/8270	10	U	10	U	10	U	10	U	10	U	10	U	10	U	
Miscellaneous Organics																	
1,2,4,5-Tetrachlorobenzen	2.0 - 20	M.1625/8270	47	U	56	U	57	U	63	U	53	U	43.4	U	54	U	
Pentabromodiphenyl ether	2.0 - 20	M.1625/8270	55	U	110	U	130	U	110	U	99	U	110	U	140	U	
Pesticides																	
4-nonylphenol (branched)	2.0 - 20	M.1625/8270	11	U	23	U	30	U	30	U	27	U	23.3	U	27.4	U	
Biphenyl	2.0 - 20	M.1625/8270	22	J	21	J	41		21	J	11	J	36	J	17.2	J	
Dacthal	0.1 - 1.0	M.8081	1	U	1	U	1	U	1	U	1	U	1	U	1	U	
Endosulfan I	0.1 - 1.0	M.8081	0.5	U	0.5	U	0.5	U	0.5	U	0.5	U	0.5	U	0.5	U	
Endosulfan II	0.1 - 1.0	M.8081	1	U	1	U	1	U	1	U	1	U	1.1	U	1.1	U	
Kelthane	1.0 - 10	M.8081	1	U	1.6	U	5.3	U	1	U	2.5	U	2.7	U	1.9	U	
Oxadiazon	2.0 - 10	M.8081	1	U	1	U	1	U	1	U	1	U	1	U	1	U	
Trifluralin	1.0 - 5.0	M.8081	1	U	1	U	1	U	1	U	1	U	1	U	1	U	
Tetraethyltin	6	M.1625/8270	47	U	56	U	57	U	63	U	53	U	43	U	54	U	

Notes:

Metals reported in mg/kg (dry weight).

Organics reported inug/kg (dry weight).

U - Undetected at concentration shown.

J - Estimated value.

* - Not analyzed due to PSDDA's environmental assessment objectives.

chromatographic cleanup techniques are different in their abilities to retain (or exclude) chemical class fractions (e.g., polar functional groups).

Using EPA method 8081 (GC/ECD), toxaphene reporting limits missed the DMMP's TDLs by two-fold (Table 1). Technical toxaphene is a multi-component mixture and shows poor chromatographic response (particularly at low concentrations). As a result the analyst must set the instrument's initial calibration for toxaphene analysis at a higher level than other pesticides. The result is a higher reporting limit

Parathion reporting limits were off by an order of magnitude from the DMMP's TDLs (Table 1). This was attributed to analyzing the extracts by the GC/MS (EPA method 1625) approach rather than the routine screening technique of Method 8141 or Method 8081. Although recoveries were excellent from the isotope dilution technique which validated the parathion concentrations (i.e., non-detects) within an 8270C scan, the weakness of the analysis is the fact that the instrument's initial calibration is 10 times higher than that of a specificity scan (e.g., EPA method 8141). Thus, a higher reporting limit is reported for the analysis of parathion.

5.1.3 Semivolatiles

Generally, the semivolatile compounds of interest were reported as being non-detects, with the exception of polyaromatic hydrocarbon (PAH) compounds. Anthracene, benzo(a)anthracene, benzo(e)pyrene, biphenyl, perylene, and pyrene concentrations were reported for each of the seven stations (see Table 3). The highest detected PAH concentrations were associated with stations EBZ01, EBS04, EBP01, and EBP11. Results indicate elevated levels of lubricant-type petroleum products in sediments. In fact, the concentrations were high enough that pyrene concentrations had to be flagged with the "J" qualifier because exceedances in the verifiable linear calibration range had occurred during the analysis. It is likely that these PAH compounds are interfering with achieving the required DMMP limits for other COCs and driving the need to employ additional cleanup techniques and fractionated extract analysis. Biphenyl levels were also flagged but with a "J" qualifier since concentrations were less than the instrument's verifiable linear calibration range.

Excluding pentabromodiphenyl ether (PBDE), 4-nonylphenol (branched), 1,2,3,4-tetrachlorobenzene, and tetraethyltin, TDLs for semivolatile organic compounds were achieved and analyte identities were validated within a standard 8270C scan using the isotope dilution technique. Reporting limits for PBDE were higher than TDLs due to low recoveries of the labeled analog ^{13}C-pentabromodiphenylether (e.g., only a 35% recovery of this labeled analyte could be identified for this project). Additional work is needed to determine where these losses occur. Tetrachlorobenzene and 4-nonylphenol reporting limits were somewhat higher than the DMMP TDLs.

5.2 MOLPADIA INTERMEDIA TISSUES

5.2.1 Metals

Cadmium, total chromium, and hexavalent chromium concentrations (wet weight) in tissue samples were reported as non-detects at all stations, with the exception of EBB04. At this station, the total chromium concentration was 0.3 mg/kg. Excluding hexavalent chromium, all TDLs for metals were achieved using stated methods. Hexavalent chromium TDLs for tissue samples could not be reached because of background interferences similar to those described in Section 5.1.1 for sediments. The remaining metals (copper, lead, and selenium) ranged in concentration (from 0.32 - 5.64, 0.6 - 2, and 0.6 -1 mg/kg, respectively) with the highest overall concentrations reported at Station EBP01 (see Table 4).

5.2.2 Pesticides

All of the draft pesticide compounds of interest were reported as non-detects (see Table 4). With the exception of the compounds parathion and toxaphene, pesticide reporting limits were toward the lower end of the required DMMP TDLs. The isotope dilution techniques also validated quantitatively the analytes concentrations (i.e., non-detects) within the 8270C scan. However, toxaphene reporting limits (EPA method 8081 GC/ECD) exceeded the required DMMP TDLs by two-fold. Parathion reporting limits were off by five-fold from the required DMMP TDLs, which was attributed to analyzing the extracts by the GC/MS approach (isotope dilution technique). The recoveries were in the acceptable ranges from the isotope dilution technique, quantitatively validating the parathion concentrations (i.e., non-detects) within a 8270C scan. The weakness of the analysis, however, is in the instrument's initial calibration being 10 times higher than that of a specificity scan (e.g., using GC/Flame photometric or nitrogen/phosphate-specific detectors). Thus, the DMMP's TDLs could be achieved using EPA methods 8081 or 8141.

5.2.3 Semivolatiles

Generally, the semivolatile organic compounds in tissue samples were reported as non-detects, with the exception of PAH compounds. Benzo(a)anthracene, benzo(e)pyrene, perylene, and pyrene concentrations were "J" qualified (see Table 4) because the instrument's verifiable linear calibration range was not attained during the analysis for this category of compounds. Excluding Pentabromodiphenyl ether (PBDE), TDLs for semivolatile organic compounds in tissue were achieved using the isotope dilution technique. Reporting limits for PBDE were higher than desired due to low recoveries of the labeled analog ^{13}C-Pentabromodiphenylether (e.g., only a 35% recovery of this labeled analyte could be identified during the analysis). Additional work is needed to determine where the losses occur.

Table 4. Tissue BCOC Concentrations in 2002 Elliott Bay Samples.

Parameter	Proposed PSDDA Tissue BT	Method	EBS02 Onsite		EBS04 Onsite		EBP01 Perimeter		*EBP03 Perimeter	*EBP07 Perimeter	*EBP11 Perimeter	EBB04 Benchmark	
Total Lipids (percent)	----	Bligh & Dyer	0.15		0.15		0.12					0.18	
PRIMARY ANALYTES													
Metals													
Cadmium	0.04	M.7131A	0.04	U	0.04	U	0.04	U				0.04	U
Chromium (total)	0.5	M.6010B	0.1	U	0.1	U	0.1	U				0.3	
Copper	0.5	M.6010B	0.32		0.47		5.64					2.2	
Lead	0.1	M.7421	0.6		1		2					0.8	
Selenium	0.2	M.7740	0.6		0.8		1					0.8	
PAHs													
Anthracene	5.0 - 50	M.1625/8270	41	U	40	U	42.1	U				42	U
Benzo(a)anthracene	5.0 - 50	M.1625/8270	39	U	38	U	4.6	J				60	U
Pyrene	5.0 - 50	M.1625/8270	14	J	9	J	42.1	U				3	J
Pesticides													
alpha-BHC	0.25 - 2.5	M.8081	1.2	U	1.2	U	1.2	U				1.2	U
Endrin	0.5 - 5.0	M.8081	2.5	U	2.5	U	2.5	U				2.5	U
gamma-BHC	0.25 - 2.5	M.8081	1.2	U	1.2	U	1.2	U				1.2	U
Heptaclor expoxide	0.5 - 5.0	M.8081	1.2	U	1.2	U	1.2	U				1.2	U
Parathion	5	M.1625/8270	26.4	U	24.9	U	29.5	U				24	U
Toxaphene	12 - 125	M.8081	248	U	247	U	249	U				247	U
CANDIDATE ANALYTES													
Metals													
Chromium VI	0.05 - 0.2	SM3500-moc	0.11	U	0.11	U	0.11	U				0.11	U
HPAHs													
Benzo(e)pyrene	5.0 - 50	M.1625/8270	11	J	11	J	10	J				4	J
Perylene	5.0 - 50	M.1625/8270	11	J	9	J	8	J				42	U
Polychlorinated naphthalenes (Halowaxes)													
Trichloronaphthalenes	5.0 - 50	M.1625/8270	5	U	5	U	5	U				10	U
Tetrachloronaphthalenes	5.0 - 50	M.1625/8270	5	U	5	U	5	U				10	U
Pentachloronaphthalenes	5.0 - 50	M.1625/8270	5	U	5	U	5	U				10	U
Hexachloronaphthalenes	5.0 - 50	M.1625/8270	5	U	5	U	5	U				10	U
Heptachloronaphthalenes	5.0 - 50	M.1625/8270	5	U	5	U	5	U				10	U
Octachloronaphthalenes	5.0 - 50	M.1625/8270	5	U	5	U	5	U				10	U
Miscellaneous Organics													

Table 4. Tissue BCOC Concentrations in 2002 Elliott Bay Samples.

Parameter	Proposed PSDDA Tissue BT	Method	EBS02 Onsite		EBS04 Onsite		EBP01 Perimeter		*EBP03 Perimeter	*EBP07 Perimeter	*EBP11 Perimeter	EBB04 Benchmark	
1,2,4,5-Tetrachlorobenzene	5.0 - 50	M.1625/8270	24.9	U	24	U	22.4	U				22	U
Pentabromodiphenyl ether	5.0 - 50	M.1625/8270	78	U	76	U	73	U				73	U
Pesticides													
4-nonylphenol (branched)	5.0 - 50	M.1625/8270	21	U	20	U	19.3	U				18	U
Biphenyl	5.0 - 50	M.1625/8270	35.7	U	34	U	32.9	U				33	U
Dacthal	0.25 - 2.5	M.8081	2.5	U	2.5	U	2.5	U				2.5	U
Endosulfan I	0.25 - 2.5	M.8081	1.2	U	1.2	U	1.2	U				1.2	U
Endosulfan II	0.25 - 2.5	M.8081	2.5	U	2.5	U	2.5	U				2.5	U
Kelthane	2.5 - 25	M.8081	2.5	U	2.5	U	2.5	U				2.5	U
Oxadiazon	5.0 - 20	M.8081	2.5	U	2.5	U	2.5	U				2.5	U
Trifluralin	2.0 - 20	M.8081	2.5	U	2.5	U	2.5	U				2.5	U
Tetraethyltin	50	M.1625/8270	24.9	U	24	U	22.4	U				22	U

Notes:

Metals reported in mg/kg (wet weight).

Organics reported in ug/kg (wet weight).

U - Undetected at concentration shown.

J - Estimated value.

* - *M. intermedia* populations are not present at station.

6.0 CONCLUSIONS

This study has demonstrated that the target trace metals and organic compounds measured in this study can be adequately quantified using routine solid waste methods with simple modifications (e.g., increasing sample volume and special clean-ups). Furthermore, the semi-volatile data for sediments and tissues were verified using two independent methods (isotope dilution technique and routine solid waste methods). The analytical applications (e.g., extractions, preparations, raw/fractionated analysis) were generally successful in achieving the DMMP's target detection limits in light of matrix interferences. Suggestions for analytical improvements are identified for the following analytes:

- **Parathion**. Reporting limits would be improved by analyzing extracts using a specific detector (e.g., EPA method 8141 using GC/NP or GC/FPD (flame photometric detector))

- **Tetraethyltin.** Reporting limits would be improved by analyzing extracts using and GC/MS-SIM methods. Differences between GC/MS-SIM and GC/MS analysis is that the GC/MS-SIM initial calibration is 10 times lower; scan is at a narrower range of masses, providing more sensitivity/specificity toward the questionable analytes (i.e., longer residence time per mass influences the ability to count more ions); and voltage to the electron multiplier can be increased to allow for more area counts (increase analyte's sensitivity).

- **Toxaphene, 4-nonylphenol, and tetrachlorobenzene**. Reporting limits could be lowered by using selective extract cleanup techniques (e.g., specifically the normal phase chromatographic cleanup technique) to enrich /concentrate these target analytes and minimize interferences. Additionally, high-volume injection (i.e., injecting more extract on column), and lowering the instrument's calibration curve (a "limited" tactic) may aid in achieving the required DMMP detection levels.

- **Hexavalent chromium**. Reporting limits could be improved by increasing the current sample size required for conducting extractions. In addition, because hexavalent chromium quickly reduces to the trivalent state in the presence of naturally occurring organics, holding times should be shortened to 48 hours. Additionally, an alternative extraction method to that used (alkaline digestion) should be developed to limit the reduction of hexavalent chromium to the trivalent state.

- **Pentabromodiphenyl ether**. Recoveries may be improved by analyzing the polar fraction extracts. However, the degree to which this change would improve reporting limits is yet to be determined.

Additional recommendations for future revisions to the development of bioaccumulative chemicals in the DMMP monitoring program include:

- Identify a higher-trophic organism to be used as the indicator species for assessment of BCOCs at disposal sites. Such an organism should have a higher lipid content than that of the sea cucumber, *Molpadia intermedia* (e.g., for this project, lipid content ranged from 0.12 to 0.18 % on the tested organism).
- Review Puget Sound Superfund data and/or historical investigative projects [i.e., Metro's Duwamish River studies, TPPS (Central Sound) and Seahurst projects (Commencement Bay), UBATS, CSO studies, etc.] to determine the frequency of detected List 1 and List 2 BCOCs. These programs have data of tentatively identified compounds.
- Look for occurrence of other bioaccumulative chemicals [e.g., from EPA's list of Important Bioaccumulative Compounds (EPA 2000b)] and their frequency of occurrence in existing data sets from sediments near or adjacent to urban embayments, combined storm and collection systems, and outfalls in the Puget Sound region.

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